Journal of Molecular Structure 1138 (2017) 198–207

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Molecular dynamics simulations of stability at the early stages of silica materials preparation

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ARTICLE INFO

Article history:
Received 26 December 2016
Received in revised form
5 March 2017
Accepted 6 March 2017
Available online 7 March 2017

Keywords:
Molecular dynamics simulations
Stability
Amorphous silica
Colloidal solution
Mean squared displacement
Radial distribution function

ABSTRACT

The main objective of this article is the Molecular dynamics simulations of stability phenomenon at the early stages of silica production in a colloidal solution. The Dreiding force field used during the whole calculation for the search of all bonding, angle, dihedral, inversion potential sets for a given configuration. For studying the stability phenomenon, two scenarios are specified: (1) The diameter of silica nanoparticles in each simulation box is the same while initial distances of two silica nanoparticles are different (system I), (2) The initial distance between two silica nanoparticles in each simulation box is the same while silica nanoparticles diameters are different (system II). The charge of atoms in silica nanoparticles determined using density functional theory calculations ($Dmol^3$). The Born repulsion forces were predominant rather than the van der Waals attraction forces. Furthermore, trajectories, mean squared displacements, radial distribution functions, and electrical charges of silica nanoparticles are determined. The displacement of silica nanoparticles was negligible which demonstrates that atoms could not approach more close. The studied colloidal solution was stable regard to the results of molecular dynamics simulations.

1. Introduction

Research on the nucleation, growth, aggregation and stability of colloidal solutions is relatively rare due to the limitations of experimental methods. In the past decades, enormous researches have been carried out in the field of silica nanoparticles through experiments and theoretical simulations. The reasons of these attempts are the vast applications of silica in different areas such as electronic devices, food and pharmaceutical industries. For instance biosensors, enzyme supporters, controlled drug release and delivery [1–3]. Moreover, researches and experiments demonstrated that silica nanoparticles have unique catalytic properties because of differences between their specific structures from the bulk. Currently, Silica nanoparticles produce experimentally through different techniques such as sol-gel, gas-phase chemical reaction, precipitation, etc. [4–6] The precipitation method is more economical and favorable one than others.

Research in the field of stability or aggregation of the nanoparticles is an interesting topic in various subjects such as precipitation, sediment formation, crystallization, solid-liquid separation, microbe and cell growth. A stable colloidal solution contains particles with the diameters from 1 to 1000 nm are capable of remaining distributed all the time. Many investigations have implemented to explore the configurations of the stable colloidal solutions, kinetics and figured out the effects of factors such as the solution chemistry on stability or aggregation phenomena [7–10].

A huge part of stability explorations conducted on clusters of nanoparticles (large nanoparticles, D = 5–100 nm) [11,12]. Investigations on stability process of small nanoparticles (D < 5 nm), especially in a colloidal solution can be helpful to the understanding of scale effect, interfacial structure and interactions between particle–particle and particle-solvent. Prediction of nanoparticle movements requires a comprehensive knowledge of mutual forces between nanoparticles including the van der Waals (vdW) attractions, Born repulsions, and electrostatic interactions [13]. The vdW attractive forces between particles can be measured through the Hamaker approach [14], Lifshitz's continuum theory [15,16], or Derjaguin–Muller– Toporov (DMT)'s approximation [17]. Numerous researches have been done in the field of stability in different industries. Ibragimova studied the stability of protein [12] and Goicochea investigated the stability of a TiO_2 dispersion using

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http://dx.doi.org/10.1016/j.molstruc.2017.03.021
0022-2860/

molecular dynamics (MD) simulations [18]. Jing investigated the stability of TiO_2 nanoparticles in water [19]. Their results show that the stability of nanoparticles in colloidal solutions influenced by the particle size. Sun investigated interaction forces between two silica nanoparticles via molecular dynamics simulations and their results compared with Hamaker approach. They found Coulomb's law is valid for calculation of electrostatic potential [20].

Computer MD simulations may help researchers to overcome the difficulties of experiments and evaluation of experimental feasibility. These computational simulations have a prominent role in the investigations of material properties and make examinations more efficient. Furthermore, understanding of processes at the atomistic level is possible just via computer simulations. Some research works have been done using MD simulations to study the microstructure of amorphous SiO_2 nanoparticles in colloidal solutions. Van Hoang used MD simulations to study the structural properties of silica nanoparticles via radial distribution functions, mean interatomic distances, coordination numbers, and bond-angle distributions [21]. Su et al. calculated normal contact and noncontact forces between two silica nanoparticles in a Lennard–Jones liquid via MD simulations [2,20,22].

Our research group synthesized SiO_2 nanoparticles through a novel process using the combination of a micro-reactor and a stirred-tank reactor for the controlled preparation of silica materials with a large pore volume and narrow-pore-diameter distribution. The schematic diagrams of the experimental device and SiO_2 preparation strategy are shown in experimental section. The novelty of mentioned preparation method is using a unique membrane dispersion microreactor [23–25]. The SiO_2 production reaction is described as

$$Na_2O\cdot 3.5SiO_2 + H_2SO_4 \rightarrow 3.5SiO_2 + H_2O + Na_2SO_4 \quad (1)$$

Dimer and cyclic are produced from silicic acid monomers through condensation when the dispersed fluid (H_2SO_4) and the continuous fluid ($Na_2O\cdot 3.5SiO_2$) solutions come into contact as the reactants at 70 °C. Dimer and cyclic polymers form in the early stages of SiO_2 production and are stable for a long time if the concentration is less than 100 ppm SiO_2 [26]. The silicic acid species grow to 2 nm, and the nucleus appears. The nuclei further grow until aggregation and gelling happen to form silica gels. Before aggregation and gelation processes nuclei are in the stable conditions. The gels disperse in a solvent after aging and washing processes due to spray drying. Microstructure in the membrane dispersion reactor determines the mixing time. Homogeneous supersaturation is achievable due to excellent mass transfer efficiency and therefore, the size distribution of the nanoparticles is controllable very well. The pH value of the SiO_2 suspension is recorded to be 8.4 [24,25,27]. The main object of this study is to model silica nanoparticles stability which produces through precipitation method using MD simulations. In the present work, MD simulations are used to find new insights into structure and dynamics of the SiO_2 nanoparticles stability processes in the colloidal solutions. Some amorphous cells constructed to evaluation changes of distances and diameters of two silica nanoparticles. Silica nanoparticle displacements were simulated and explored quantitatively at atomistic or molecule scale through an atomistic trajectory, and adsorption of water molecules. In other words, the main focus of this paper is in relative motion (attraction/repulsion) between nanoparticles simulated in a salty medium during the simulation.

To the best of our knowledge, many studies carried out on the stability of small and large nanoparticles such as TiO_2 while there are just a few investigations about the stability of SiO_2 nanoparticles. In addition, a large portion of researches done on the crystalline form of silica instead of amorphous structure. Therefore, this research work is the first one and can be promising one for future works on the stability of silica nanoparticles smaller than 4 nm and amorphous structure.

This paper is prepared in two major sections. First, preparation of silica nanoparticles using precipitation method in the laboratory is described briefly. Second, the stability phenomenon investigated theoretically using molecular dynamics simulations. Two stability and aggregation phenomena at the early and late stages of silica materials preparation occur, respectively. Theoretical investigation of stability step carried out in this paper while simulation of aggregation step at the late stages will implement as a future research work.

2. Experimental section

As stated in the last section, our research group synthesized SiO_2 nanoparticles through a novel process which is described briefly in the following. The membrane dispersion microreactor mainly consisted of two stainless steel sample plates (40 mm × 40 mm × 10 mm) and a stainless steel microfiltration membrane. Fig. 1 shows the experimental device, the strategy of the preparation of SiO_2 nanoparticles and structural diagram of the membrane dispersion micromixer. A distribution room and a cross flow channel were separately machined on two sample plates by a laser cutting machine (LM50D, LAJAMIN). The stainless steel microfiltration membrane (Zhen Yuan Purification Technology Co., Ltd.) with a pore size of 5 μm was placed between the distribution room and the cross flow channel as the dispersion medium. The geometric size of the microchannel was 12 mm × 4 mm × 1 mm. The acidification reactor was a three-necked, round-bottomed flask with continuous agitation. The two reactors were placed in the hot water bath and connected via a plastic tubing with a diameter of 8 mm.

The reactants included industrial water glass ($Na_2O\cdot 3.5SiO_2$, Yuanxiang Chemical Co., Ltd.) and Sulfuric acid (H_2SO_4, Beijing Modern Eastern Fine Chemical Co., Ltd.). The continuous fluid $Na_2O\cdot 3.5SiO_2$ solution was mixed with the dispersed fluid H_2SO_4 solution in the membrane dispersion microreactor at 70 °C. When the two fluids came into contact with each other, SiO_2 gels were synthesized and were immediately delivered to a stirred tank reactor. The gels were dispersed in water. Then the resulting slurry was kept aging for 2 h at 70 °C, suction filtered, washed three times with distilled water, dispersed in a solvent (water, ethanol or PVA solution) and dried with a spray dryer (L117, Laing Scientific Co., Ltd.). The slurry was injected by a nozzle with a tip diameter of 0.7 mm and rapidly dried by preheated air.

3. Theoretical method

3.1. Constructing of amorphous SiO_2 nanoparticles and simulation systems

The SiO_2 nanoparticles were generated from α-quartz which has a hexagonal symmetry structure belonging to P3121space group with the unit cell parameters of a = 4.91 Å, c = 5.40 Å and a density of 2.65 g/cm^3 [28]. All available structures of SiO_2 were compared to find the one with the lowest energy. Consequently, the α-quartz with stable structure was chosen for constructing SiO_2 nanoparticles, as was expected. Each unit cell has six oxygen and three silicon atoms, four types of O–O distances and two types of Si–O bond lengths. The SiO_2 nanoparticles with different diameters were constructed by cutting out atoms from silica crystal. Snapshots of the 1 and 2 nm SiO_2 nanoparticles have been shown in Fig. 2.

The structural defects at their surfaces are clearly observable.